



Research paper

Influence of metahalloysite on mitigating alkali-aggregate reaction in concrete

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Abstract: The durability of concrete structures can be compromised by alkali-aggregate reaction, a chemical process between the alkalis and reactive minerals within the aggregate. The reaction produces a gel of hydrated sodium-potassium-calcium silicate that expands in the concrete, deteriorating it. Adding mineral admixtures to concrete is recognized as a highly effective strategy to mitigate expansion due to alkali-aggregate reactions. This study investigated the use of a natural mineral admixture, metahalloysite, to mitigate the reaction effects. Expansion tests were conducted according to ASTM C441. The microstructure of the expanded specimens was examined using computed tomography and scanning electron microscopy coupled with X-ray microanalysis. The results showed that the 25% cement substitution with metahalloysite significantly lowered the swelling of the concrete specimens, keeping it within safe limits. Microstructural examination of the specimens without admixture showed numerous cracks in the aggregate grains, the presence of reaction products, and ettringite crystals. Specimens with admixture showed the presence of non-swelling sodium-potassium silicate gel and a dense C–S–H phase with a reduced C/S ratio.

Keywords: alkali-silica reaction, expansion, metahalloysite addition, microstructure

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1. Introduction

The alkali-silica reaction (ASR) is an undesirable reaction in concrete that occurs between reactive minerals in the aggregate and the pore solution containing sodium and potassium ions. The product of this reaction is a sodium-potassium-calcium silicate gel that swells under the influence of water absorption, causing concrete degradation. This reaction permeates the entire concrete volume because the necessary components are inherent to the concrete, not dependent on external factors. Numerous studies have been conducted to understand the physicochemical mechanisms of the alkali-silica reaction [1–4]. Its occurrence directly reduces concrete durability, and, in addition, concrete cracking significantly favors other corrosion processes. The extensive research efforts on alkaline corrosion in concrete underline its ongoing significance. This is further reflected by the numerous projects and recurring international congresses held since the 1950s. Also in Poland, the topic of aggregate reactivity is widely studied, as confirmed by multiple publications [5–8], as well as the project “ASR-RID: Alkali reactivity of domestic aggregates”, the aim of which was to develop technical guidelines for designing high-durability concretes, with particular attention to protection against damage caused by the reaction between alkalis and reactive minerals in the aggregate [9]. Recently, attempts to use waste glass as a partial replacement for aggregate in concrete have become popular [10]. As the authors themselves noted despite the many advantages of such a solution, an important aspect that requires attention is the possibility of alkali-aggregate reactions. It is crucial to conduct research focusing on ways to eliminate the effects of ASR.

Several strategies can be employed to minimize the occurrence of undesirable volume changes in concrete. These include utilizing low-sodium and potassium cements, limiting water access to concrete structural members, lowering the cement content, incorporating non-reactive aggregates, and finally, utilizing mineral admixtures and/or chemical additives. Preventing ASR at the design stage of concrete mix formulation is crucial. Among the various mitigation strategies, mineral admixtures have emerged as a particularly effective approach for controlling ASR-induced concrete expansion [4]. Mineral admixtures derived from industrial byproducts, such as granulated blast furnace slag (hydraulic admixture) and fly ash and silica fume (pozzolanic admixtures), have proven effective in mitigating ASR. Highly reactive silica-rich mineral admixtures, like silica fume, can effectively suppress expansion at relatively low dosages (10–15%), while granulated blast furnace slag requires higher replacement levels (above 50%) [11–13]. The optimal dosage of mineral admixtures depends on their specific properties, including mineral and chemical composition, aggregate reactivity, concrete alkali content, and exposure conditions [14, 15]. The availability of industrial byproducts may be constrained due to environmental concerns and efforts to reduce coal combustion. Additionally, the quality of these admixtures can vary, prompting the exploration of natural alternatives. Natural mineral admixtures with pozzolanic properties include calcined clays, zeolites, perlite, and pumice. Numerous studies have demonstrated the beneficial effects of natural pozzolans in mitigating ASR when used in appropriate quantities [16–18]. Among natural mineral admixtures, metakaolin, a calcined clay, has been extensively studied and exhibits remarkable effectiveness in controlling ASR at an admixture content of approximately 15%.

Natural mineral admixtures effectively control ASR by participating in pozzolanic reactions, forming C–S–H phases capable of incorporating sodium (Na^+) and potassium (K^+) ions. This reduces their concentration in the concrete pore solution, thereby limiting their availability for reaction with reactive aggregates. The capacity of the C–S–H phase to bind sodium and potassium ions is associated with a lower C/S ratio [14]. Metahalloysite, obtained through the calcination of halloysite, is a promising natural mineral admixture with pozzolanic properties [19]. However, comprehensive investigations into its application as a concrete admixture to mitigate ASR are still lacking.

This study investigates the influence of metahalloysite additives in cement on mitigating ASR-induced expansion. The testing was conducted in accordance with ASTM C441, replacing 25% of the cement with metahalloysite and employing borosilicate glass as the reactive aggregate.

2. Materials and methods

Portland cement CEM I 42.5R with a sodium oxide equivalent of 0.76% was used for preparing the specimens. The specific surface area of the cement determined by the Blaine method was $3240 \text{ cm}^2/\text{g}$. Borosilicate glass was used as the aggregate. Following ASTM C441 guidelines, the glass was crushed to the specified particle size fractions and added to the mortar in appropriate proportions. The particle size distribution is shown in Fig. 1. The average particle size of the cement was $11.88 \mu\text{m}$.

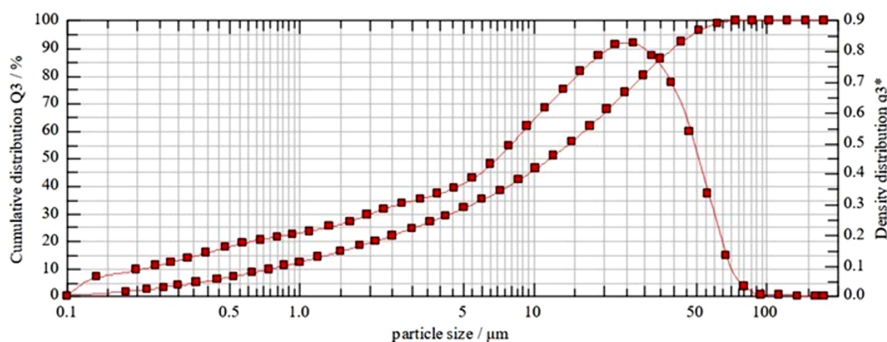


Fig. 1. Cement gradation chart

Metahalloysite was employed as the cement admixture. It was prepared by dehydroxylating halloysite at 750°C for 2 hours. The halloysite was obtained from the Dunino quarry near Legnica, Poland. The particle size distribution is shown in Fig. 2. The average particle size of the metahalloysite was $7.82 \mu\text{m}$.

The particle size distributions of metahalloysite and cement were measured using a HELOS KR laser diffractometer. The chemical composition of metahalloysite and cement was determined using X-ray fluorescence (XRF) analysis. The chemical composition of the cement and metahalloysite is presented in Table 1.

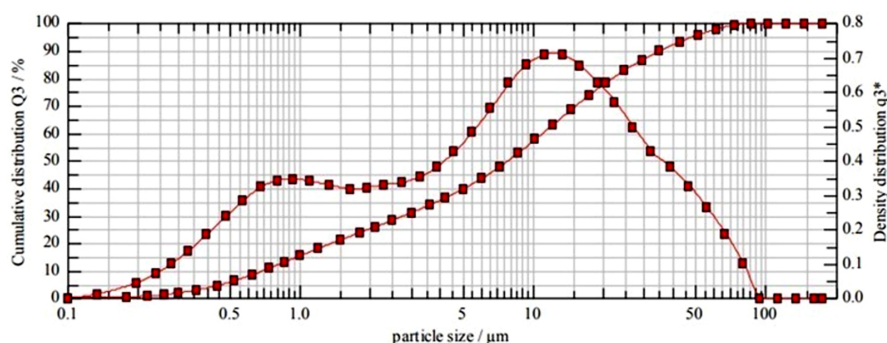


Fig. 2. Metahalloysite gradation chart

Table 1. Chemical composition of cement and metahalloysite

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	Mn ₂ O ₃	ZnO	Cr ₂ O ₃
Cement	18.96	5.19	2.77	62.03	1.60	3.15	0.84	0.21	–	–	–	–	–
Metahalloysite	26.97	21.40	35.01	1.12	6.09	0.02	0.11	0.16	7.70	0.84	0.36	0.04	0.13

The mortar expansion tests were conducted in accordance with ASTM C441 [20]. This standard evaluates the effectiveness of mineral admixtures in preventing ASR-induced expansion. The expansion testing period was extended to 240 days. Two series of mortar bars with dimensions of 25 × 25 × 250 mm were prepared. The first series was made without any admixture (OPC), while in the second series (25%MH), 25% of the cement was replaced with metahalloysite. The dry mortar ingredients were mixed in a ratio of 1 part binder to 2.25 parts aggregate, and the water-to-cement (w/c) ratio was 0.5. After 24 hours of curing, the mortar specimens were stored at 38°C above water. Linear length changes of the specimens were measured using a Graff–Kaufman apparatus. The initial length measurement was performed immediately after demolding, and subsequent measurements were made at 14 days, and one, two, three, four, five, six, seven, and eight months. Microstructural observations of the specimens were conducted using Nikon XT H 225 ST computed microtomography (μCT) and scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) in a QUANTA 250 FEG microscope.

3. Results and discussion

Figure 3 shows the results of mortar bar elongation measurements.

The mortar specimens prepared with only Portland cement (OPC) exhibited the highest expansion rate in the initial testing period. However, their expansion stabilized at 84 days. In contrast, the specimens incorporating 25% metahalloysite admixture (25%MH) showed no expansion. Instead, they experienced a slight initial shrinkage. The researchers proposed a limit of 0.10% expansion at 56 days as a benchmark for the ASTM C441 test method [21].

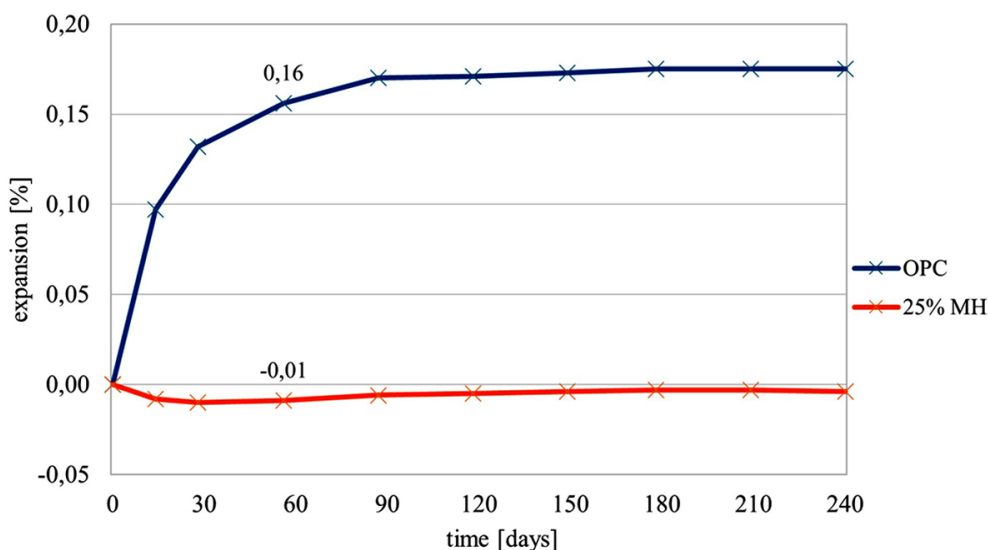


Fig. 3. Expansion of mortar specimens prepared with Portland cement (OPC) and Portland cement with 25% Metahalloysite Admixture (25% MH) according to ASTM C441

The ASTM C1157 [22] standard, which specifies requirements for cements, sets stricter limits: 0.02% expansion at 14 days and 0.06% expansion at 56 days. The results strongly indicate that metahalloysite, when employed as a mineral admixture in cement, effectively mitigates ASR-induced expansion. Mortar specimens containing 25% metahalloysite exhibited no expansion, meeting the stringent requirements of ASTM C1157 for cements with admixtures.

After measuring the linear elongation of the specimens at 56 days, their microstructure was analyzed using computed tomography. This non-destructive technique allowed for examining voids within the specimens without damaging them or interrupting the expansion tests. Following the scans, the specimens were placed in containers and stored in a climate chamber at 38°C. Figure 4 presents CT images of the internal microstructure of the specimens.

Less dense areas, such as air pores, appear as darker regions in the CT image. In contrast, higher density areas appear as lighter regions. Figure 4a, showing a cross-section of the OPC specimen, reveals pores that are either fully or partially filled with gel, an ASR product. Examples of where the gel is present in the pores are marked with a red border. The image of the 25%MH specimen (Fig. 4b) shows no visible gel formation within the pores.

Figures 5–8 show mortar specimen microstructures after 240 days of expansion, observed using a scanning microscope, and X-ray analysis results for selected micro areas.

SEM analysis confirmed the presence of cracked aggregate grains and potassium-calcium silicate gel in the OPC specimens (Fig. 5a), on the surface of the cracked aggregate grains and in the air voids (EDS analysis in micro area 1, Fig. 5b). Analysis in micro area 2 revealed the presence of cement paste (Fig. 5c). Figure 6 shows ettringite crystals within the cracks and air voids of the OPC mortar specimens.

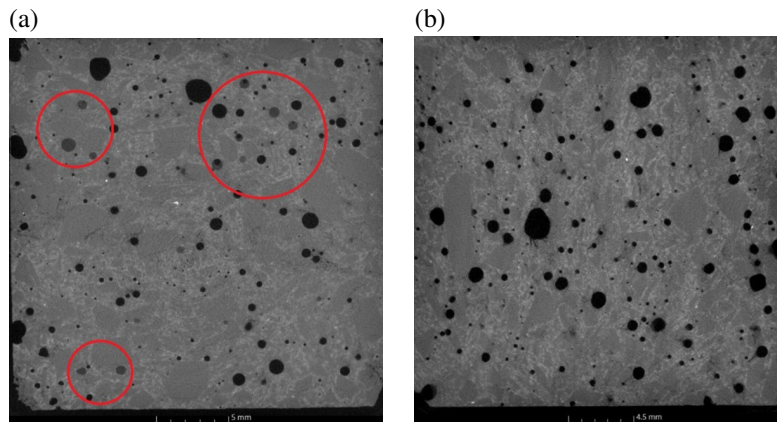


Fig. 4. CT images of mortar specimens in cross-section: (a) specimen without admixture, (b) specimen with 25% metahalloysite admixture

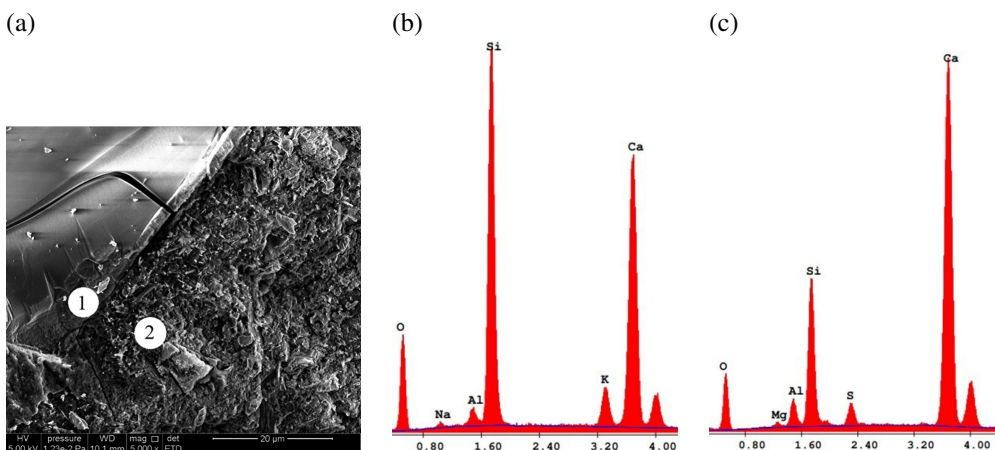


Fig. 5. (a) cracks in the aggregate grains of the OPC specimen, (b), (c) EDS analysis in micro areas 1 and 2

The incorporation of sodium and potassium ions into the sodium-potassium-calcium silicate gel, a product of the alkali-silica reaction (ASR), decreases the pH of the concrete pore solution. This pH reduction promotes the release of sulfate ions from the C–S–H phase and contributes to the formation of secondary ettringite [23].

It is likely that the formation of ASR gel and cracks caused by the reaction of alkalis with aggregates results in a decrease in the concentration of potassium and sodium ions in the pore solution, which favors the recrystallization of ettringite. This formation type suggests that ettringite is not the direct cause of damage [24].

Figure 7 and Fig. 8 show the microstructure of the metahalloysite-admixed specimen.

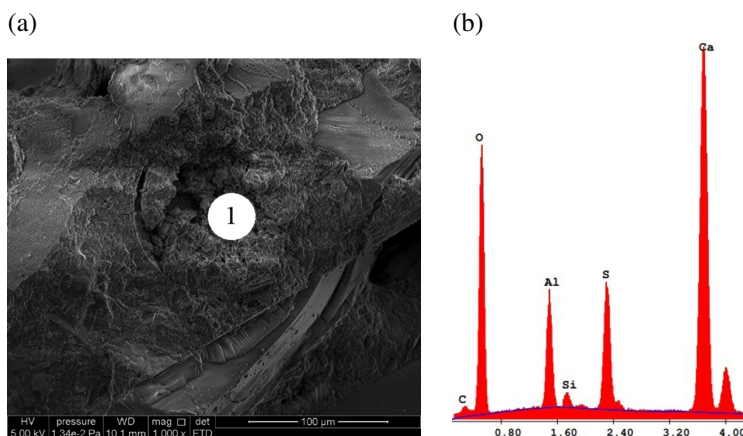


Fig. 6. (a) Air void in the mortar without the admixture, filled with ettringite, (b) EDS analysis at point 1

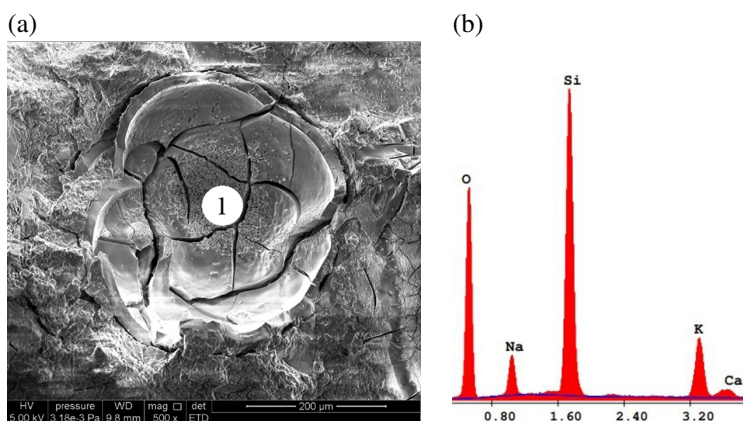


Fig. 7. (a) Sodium-potassium-calcium silicate gel in metahalloysite mortar, (b) gel composition – EDS analysis at point 1

The mortar specimen containing metahalloysite exhibits a limited amount of gel formation, primarily confined to air voids (Fig. 7). Varied gel compositions were observed; the metahalloysite gel contains a lower proportion of calcium and a higher proportion of sodium and potassium. The sodium-potassium silicate gel with low calcium content is characterized by its non-swelling properties.

The microstructure of the metahalloysite-admixed mortar specimen, as shown in Fig. 8a and 8b, revealed a dense C–S–H phase. The EDS microanalysis in points 1 and 2 (Fig. 8c and 8d) provided insights into the elemental composition of the C–S–H phase in the metahalloysite mortar. The analysis revealed a reduced C/S ratio compared to the OPC mortar. This observation suggests that the metahalloysite may promote a pozzolanic reaction, leading to the consumption

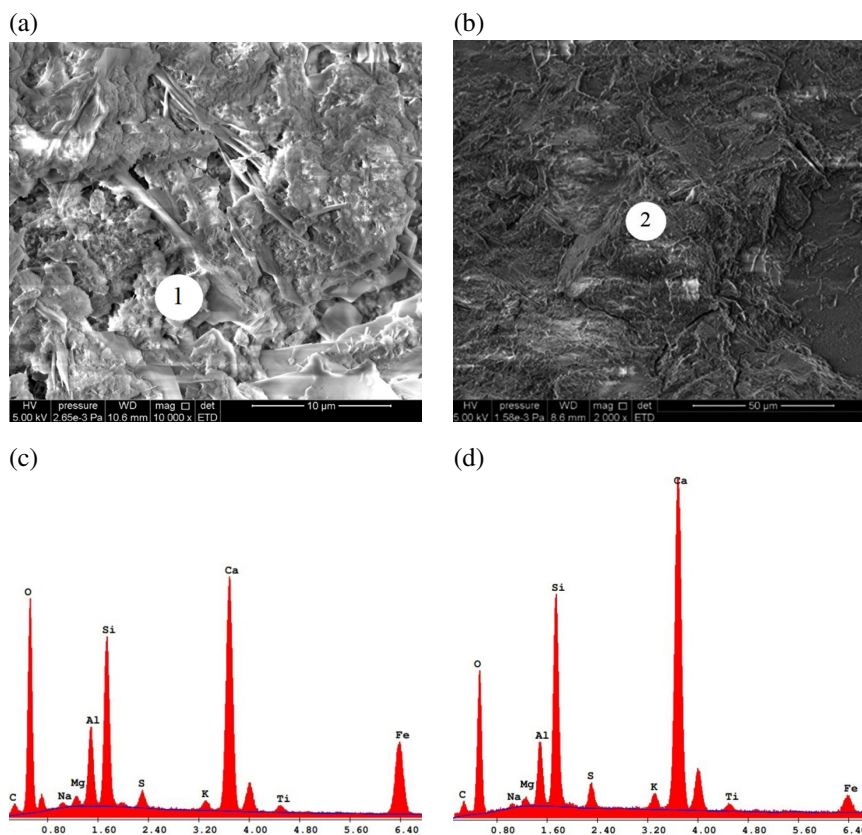


Fig. 8. (a), (b) microstructure of the metahalloysite-admixed specimen; (c), (d) EDS analysis at points 1 and 2

of portlandite. The C–S–H phase in the metahalloysite mortar also exhibited an increased iron content, likely originating from the metahalloysite particles and the presence of sodium and potassium ions. The overall observations support the hypothesis that metahalloysite can potentially mitigate the effects of the alkali-silica reaction due to the pozzolanic reaction.

4. Summary and conclusions

The study revealed the following key points:

- The addition of 25% metahalloysite to cement effectively mitigates the effects of ASR, as evidenced by the absence of expansion throughout the entire testing period.
- Microstructure observations of mortar specimens using computed tomography revealed the presence of gel in air voids within the specimens without metahalloysite admixture.

- SEM observations and micro-area X-ray analysis (EDS) of mortar specimens without metahalloysite revealed numerous cracks in aggregate particles, as well as potassium-calcium silicate gel primarily present on the aggregate surface, in crack areas, and in voids. Ettringite crystals were also identified in cracks and air voids.
- The metahalloysite-admixed mortar exhibits a dense microstructure with a C–S–H phase characterized by a reduced C/S ratio. Sodium-potassium silicate gel with low calcium content, which lacks swelling properties, was observed in air voids.
- The findings of this study highlight the promising potential of metahalloysite as an effective additive for mitigating ASR in concrete. Further research is needed to optimize metahalloysite content for ASR mitigation.

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Wpływ metahaloizytu na skutki reakcji alkalia-kruszywo w betonie

Słowa kluczowe: ekspansja, dodatek metahaloizytu, mikrostruktura, reakcja alkalia-krzemionka

Streszczenie:

Jednym z czynników mogących doprowadzić do uszkodzenia konstrukcji budowlanych jest reakcja zachodząca pomiędzy alkaliowymi składnikami kruszywa w betonie. Produktem reakcji jest żel uwodnionego krzemianu sodowo-potasowo-wapniowego, który pęczniejąc wywołuje ekspansję i destrukcję betonu. Powszechnie uznaje się, że stosowanie dodatków, jest jednym z najbardziej efektywnych sposobów kontrolowania ekspansji betonu, wywołanej reakcją alkalia-krzemionka. W pracy podjęto próbę oceny metahaloizytu jako naturalnego dodatku mineralnego na ograniczanie skutków reakcji alkalia-krzemionka. Badania ekspansji przeprowadzono zgodnie z metodą ASTM C441. Na próbkach poddanych badaniom ekspansji przeprowadzono badania mikrostruktury przy wykorzystaniu tomografii komputerowej i skaningowej mikroskopii elektronowej sprzężonej z mikroanalizatorem rentgenowskim. Wyniki badań wykazały, że zastąpienie cementu metahaloizytem w ilości 25% wagowych powoduje zmniejszenie ekspansji próbek do poziomu niezagrażającego trwałości betonu. Badania mikrostruktury próbek bez dodatku wykazały liczne spękania ziaren kruszywa, obecność produktów reakcji alkalia-krzemionka oraz kryształów ettryngitu. W próbkach z dodatkiem stwierdzono obecność żelu krzemianu sodowo-potasowego niemającego zdolności pęczniejących oraz zwartej fazy C–S–H o obniżonym stosunku C/S.

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